DEVELOPING CERAMIC OPAQUE GLAZES USING BONE ASH

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ABSTRACT  
It is widely observed that refined tin oxide is greatly expensive despite its abundant availability in Nigeria. Most ceramic industries depend largely on foreign materials as opacifier rather than local materials which brought about high cost of production. As a producer of cattle, Nigeria presents a great potential of recycling cattle bone as ceramic materials and as a good source of opacifier. A comparative study made on the optical and the tactile properties of opaque glaze produced with bone ash and tin oxide on transparent glaze at different percentages proved that, 7 to 9 % of cow bone ash in transparent glaze is a good composition in achieving an opaque glaze. This study has invariably helped to convert waste to wealth and greatly reduced dependency on tin oxide as ceramic glaze opacifier which is expensive to procure.

Introduction  
Pottery is one of the oldest and most widespread of the decorative arts, consisting chiefly of functional objects (such as vessels, plates, and bowls) made of clay and hardened with heat (George, 2011). Pottery is clay products that are modelled, dried, and fired, usually treated with glaze to make them impervious to water, hygienic and beautiful to feel. The art of embellishing clay pot with materials such as ceramic stains, oxides which when heated on the clay pot, leads to fused glasses and is of great antiquity. These ceramic glazes can be applied to the surface of clay products, and after heating, it gives a vitrified surface in form of glass.

Alasa (2005) also described glaze as a glassy coating on a ceramic wares, compounded from earthen mineral substances which after refining are mixed with water, thoroughly milled, blended and smeared on a bisque ware, then subjected to intensive heat in the kiln to melt and cover the ware; thus making it glossy hard, dense, impervious, smooth, washable, odour free, and aesthetically appealing serving both functional, aesthetic and utilitarian value. Parmelee (1947) stated that glaze may be coloured or colourless, transparent, translucent or opaque. Opaque glazes are glazes that are sufficiently low in light transparency as to effectively hide the body from direct view. They are usually white, but this is not a requirement. Opacity in glazes is caused by the reflection and refraction of light phases and particles suspended in the clear matrix. The commonest and easiest way of creating opacity according to Emodah (2006), is to use an opacifier such as Tin oxide and Zirconium oxide. Opacifiers are glaze additive that transforms a transparent glaze into an opaque one. Common opacifiers are tin oxide and zircon compounds. They typically work by simply not dissolving into the melt then, the white suspended particles reflect the light (Digitalfire, 2010).

Bone ash is the white, powdery ash left from the burning (calcination) of bones. It is primarily composed of calcium phosphate. This is also defined by Andrew (1991) as substance which is obtained by calcining bones at moderate temperature; this ash is pure white in colour. Bone ash has a
significant use in ceramics productions due to its chemical content. It has been found useful as a raw material for ceramic application and other allied industries. The calcium oxide present in bone ash gives strength and stability to ceramic wares; it also serves as a fluxing agent on high temperature glaze (Ayilaran, 2009). The phosphate present in the bone ash causes precipitation which is responsible for translucency in bone china, opacity in glazes, enhancement translucency in porcelain body due to its same refractive index as glass and serves as a stiffener for low viscous glazes.

Research has shown that bone ash can be used in some ceramic applications such as Production of Bone china, Porcelain body and Glaze composition. Bone china is made from bone ash. The initial development of bone china is attributed to Josiah Spode, who introduced it around 1800. The original basic formula of six parts bone ash, four parts china stone, and three and a half parts china clay remains the Standard English body. Bone china is extremely hard, stronger than hard-paste porcelain due to the addition of the bone ash and easier to manufacture. The use of bone ash makes bone china intensely white and allow light to pass through it (Steve Birks, 2011).

Technically, bone china is a form of hard paste porcelain because it is a mixture of clay and another non-glassy material. Braganca & Bergmann (2006), affirm Porcelains from bone ash to be widely accepted and present high market value in Brazil, although, their manufacture and research are still restricted to few countries. Brazil as a great producer of cattle, presents great potential for the recycling of cattle bone into ceramic materials especially in the production of porcelain. The higher mechanical strength and better aesthetic qualities, especially its whiteness, make bone porcelains very attractive materials in terms of industrial applications potential.

The use of bone ash in glaze compositions is not arbitrarily done but based on careful considerations as opined by Anon, (1983) and Bridges, (1976). Bone ash contain about 58% of calcium phosphate \((\text{Ca}_3 \text{PO}_4)_2\) in additions to calcium carbonate \((\text{CaCO}_3)\), fat and organic matter containing nitrogen. The chemical and physical properties of phosphorous pent oxide as reported by Ayilaran, (2005) earns for it a pre-eminent position as constituents of glazes which is essentially a group of materials characterized by low fusion points, low viscosity and with low thermal expansion coefficient, high resistance to thermal shock and durability.

Zirconium oxide is rarely found in Nigeria. Ceramists usually import it to be used in the studio and the cost of importation is very high. Tin oxide which is readily available in Nigeria is also expensive due to its usage as protective coating for copper vessels, and various metal used in manufacturing of tin cans. The use of opacifiers in tableware, dinnerware, sanitary wares and even in decorative wares is very paramount and must not be allowed to go into extinction. The quest for aesthetic satisfaction of developing opaque glazes at lower cost of production is the focus of this investigation: that is the use of bones from abattoir as an alternative opacifier to tin and zirconium oxides.

**Research Methodology**

Kothari (2007) defined research as a scientific investigation from known to unknown. This scientific method is sequential and consists of some identifiable steps such as identifying a problem, research hypothesis, population, sampling and sampling technique, collection of data and data analysis. Izedomi (2005) admitted that scientific research is directed towards acquiring information that is to contribute to knowledge so as to be able to harness available materials in the immediate environment to accomplish and resolve conflicts. This study had firmly adhered to these steps opined by Kothari (2007) in order to provide the blueprint of tackling the research problem that arose from this investigation.

This study explicitly shows the processes involved in producing a good bone ash that is carbon free, the chemical analysis of the bone ashes and how it was mixed with transparent glaze at different percentage using a simple line blend to produce opacified glaze effects.
Studio Experiment
The research design that was adopted for this study was purely studio experimental research design due to the nature of the study. The materials used to produce the opaque glaze are Kaolin, flint, whiting, and potash feldspar for the formulation of transparent glaze, which were sourced within Ijero Ekiti in Ekiti State, Akure in Ondo State and Auchi in Edo States respectively. Meanwhile bones that were experimented with the transparent glaze to create opaque glaze were sourced from Bussa Abattoir at Sagari Village in Akure. Tin oxide which was used as parallel composition to bone ash and to affirm the quality of opacity of opaque glaze produced from bone ash, was sourced from Jos in Plateau State.

The bones were then calcined and finely grounded into powder which is known as bone ash. The bone ashes were further mixed with stable transparent glaze recipes at different percentages to each other, using a simple line blend and gloss fired at 1180°C in the kiln. Tin oxide was also experimented alongside with the same transparent glaze recipe using a simple line blend which served as pure control variable to ensure that what is observed in the experimental variable does not happen by mere chance and has the same product quality as tin oxide.

Processing Bone Ash
In order to produce bone ashes that will be suitable as glaze material, the following steps were undertaken in processing the bones collected from the abattoir into bone ash;

1. Soaking and Washing of bone
2. Boiling of bone
3. Calcination of bone
4. Crushing and grinding
5. Pulverization into powder
6. Production of test tiles
7. Formulation of Transparent Glaze used

Soaking and Washing of bone: this is the act of softening and saturating the bones gathered as consequence of immersing them into water. The immersion in water was carried out in two days in order to remove dirt, soft beef and contaminants from the bones. The bones were removed from water on the third day, rinsed and were sundried. The bones were poured into a bath and were washed with sponge in order to remove adhered beef. (See plate 1)

Boiling of bone: in order to further remove impurities such as unwanted liquids in the bone marrow, clinged beef and most especially the fat present in the bone, the bones were boiled at 100°C in the water with the addition of soda potash (Na₂Al₂O₆·SiO₂) to help to soften the adhere beef for easy remover. Fats and glue were seen boiling out of the bone at 100°C and the bones were de-beefed, rinsed and sundried. See in plate 2 and 3.

Calcination: This is the process of heating a substance below its melting temperature in order to remove organic matter including chemically combined water in the substance and to create a fine network of cracks on the substance for easy grinding. By calcination, traces of carbon and small amount of water within the material are burnt out. The most important effect is to weaken the structure. Volume changes associated with the heating and cooling of the material result in the development of network of fine cracks throughout the material. At about 500°C to 600°C, chemically combined water is driven out and at about 900°C and above, most or all organic compounds are said to be totally removed (Igbinedion, 1995). The bones used for the study were calcined above 1000°C in order to ensure that all chemically combined water and organic matters are all removed.

Note: under-calcination may contain so much organic materials that result to frothing which may lead to glaze fault.

Crushing and grinding
This is the process of reducing a substance into small pieces or particles by pounding or abrading. The bones were in the grinding machine to make the bone into fine particle size. The grinding machine was not completely tightened in order to avoid the bones been contaminated with iron oxide. To achieve a pulverised or finer particle size, the bones were then ball milled using a porcelain jar in The Department of Industrial Design, Federal University of Technology, Akure. Plate 6 and 7 shows the procedure undertook to achieve the aim.
Pulverization
Pulverization is an act of grinding substances into powder or dust particle size. Glaze ingredients are usually pulverized into powder. The finer the particle size, the glossier the glaze melts on ceramic ware. Sometimes, the finer particles help to lower the eutectic point due to the surface area of the material.
Plate 8 and 9 shows how the bone used for the study was pulverized in the porcelain ball mill at The Department of Industrial Design, Federal University of Technology, Akure to make the material suitable in composing glaze recipes. The time taken to pulverize a batch of the bone took up to 12 – 24 hours.

Production of Test Tiles
Plate 10 is a picture of upright triangular test tiles made for the purpose of testing the bone ash behaviour with transparent glaze at different percentage composition. A stencil was made with printing press plate to cut out the clay slab produced into sizes and a rectangular base was given to the tiles to make them erect upright without falling easily. The tiles were allowed to dry very well before subjecting them to bisque firing. The tiles were fired between 950°C and 1050°C after drying to be hard enough to endure normal handling during glazing.

Formulation of Transparent Glaze used
The transparent glaze used for this study was from known recipe derived from studio experiment by Fatuyi, 2011 which served as a good base glaze for the study. The recipes used and their percentage compositions by part are as follow:
Feldspar 50
Whiting 25
Flint 20
Kaolin 5

Studio Experimentation & Data Analysis
The cow bone ash was mixed with a transparent glaze to compose an opacified glaze. This was done by line blending the bone ashes ranging from 1-15 % with transparent (see table 1). In other word, One percent of cow bone ash was mixed with nine – nine percent of transparent glaze until fifteen percent of cow bone ash was mixed with eighty – five percent of transparent glaze. 10grammes of each sample was prepared and each sample was thoroughly mixed with 4ml of water in order to have a uniform quantity. The same procedure was carried out for tin oxide, thereby having thirty samples in all that were tested. The samples were applied on the test tile produced using brush after mixing them properly. See plate 11 and 12. The samples were further subjected to firing using an electric kiln under a full oxidation firing atmospheric condition at 1200°C. The firing was monitored with a thermocouple and Orton cones (08, 03, 4) to ascertain the temperature.

Discussion and findings of First Firing Observation
Plate 13 shows the samples of opacified glaze produced using cow bone ash as opacifier. From the physical examination conducted on the samples, it was observed that the level of glaze melt of cow bone ash with transparent glaze is satisfactorily good without any flaw. This can be seen in the table below as the 15 (100%) samples melted very well.

Observation
It was also observed that 5 (33.33%) of cow bone ash samples out of 15 samples have low bloating, 2 (13.33%) is highly bloated and 8 (53.33%) did not bloat. It can be inferred from the observation that cow bone ash in term of glaze bloat, has a very low tendency to bloating. Though the higher the percentage increase in cow bone the higher the tendency to bloating. A good opacity that is less prone to bloating was achieved between the ranges of 7 – 9 %. See plate 13 and Table 3 below.

Observation
The physical examination of the samples of cow bone ash in terms of glaze crawl shows that 7 (46.67%) out of 15 samples have low glaze crawling, 2 (13.33%) is highly crawled and 8 (53.33%) did not crawl. As earlier stated that crawling can be attributed to the material in glaze which increases the viscosity and surface tension, it can be inferred in essence that cow bone ash is moderately viscous as glaze material and has shown low tendency to crawling when used as an opacifier with transparent glaze. See table 4 below.
Observation: - it was observed that 8 (53.33 %) samples of cow bone with transparent glaze out of 15 samples is highly opaque. 3 (20%) out of the samples were low in opacity and 4 (26.67%) were insignificantly different from transparent glaze. It can be inferred that cow bone ash is a good opacifier with transparent glaze. See plate 15 and table 5 as discussed.

Discussion and findings of Second Firing
6 samples were recomposed based on the assessment of the result of samples tested above. This test was conducted in order to improve the brilliancy of the opacified glaze samples produced from cow. 3 – 4 percentage of zinc oxide was introduced into the composition. It was observed that the introduction of zinc oxide into the composition lowers the eutectic point, increase the brilliancy of the opaque glaze in comparison to tin oxide and also remove bloating. The addition of zinc oxide to the glaze stabilizes the glaze composition and makes the result equivalent to that of tin oxide. The results were found to be very good in term of glaze crawl, glaze bloat and glaze opacity. See table 6 as discussed and plate 13 for the result of the firing.

Assessment of opacified glaze produced using tin oxide
Observation: - plate 14 is opacified glaze samples produced using tin oxide as opacifier. It was observed that tin oxide which was used as a control group has a very good glaze melt as the experimental group and did not show any sign to bloat but has traces of crawling at higher percentage. The result obtained from the control group proves that the efficiency of machines in terms of work - done is not 100%. i.e. the usage of tin oxide as opacifier is not absolutely free from flaws due to human error, but it is still the best opacifier. The degree of its opacity is very good. See table 7, 8, 9 and 10 for the analysis of the samples tested as discussed.

Comparison of Opacified Glaze produced using Cow Bone Ash and Opacified Glaze Produced using Tin Oxide in term of Glaze Melt, Glaze Bloat, Glaze Crawl and Glaze Opacity
Fifteen samples in all of tin oxide and cow bone ash melted very well. No samples bloated or crawl using tin oxide with transparent glaze ditto cow bone ash, while Fifteen samples in all of tin oxide and that of cow bone ash with transparent opacified well. This inferred that there is no significant difference between opacified glaze produced using tin oxide and opacified glaze produced using cow bone ash in terms of glaze bloat, glaze crawl and glaze opacity.

Summary of Findings
Based on the field assessment when bone ashes from cow were used as opacifier in ceramic glaze as substitute to tin oxide, the following findings were made:
1. Cow produced a good melt when used as part of glaze material mixed with transparent glaze between the ranges of 4 – 15 %.
2. Cow bones are less prone to bloating and crawling when mixed ceramic transparent glaze.
3. Cow bone produced better opacity in ceramic glaze with the addition of 7 - 9% opacifier when mixed with transparent glaze.
4. The quality/brilliance of cow bones could be improved with the addition of 3 – 4% of zinc oxide to make opaque glaze of little or no difference compare to Opaque glaze produces from tin oxide only. This had eventually reduced the cost of producing opaque glaze.
5. Cow bones produced fewer flaws when used as an opacifier on ceramic transparent glaze in respect to texture, brilliance and opacity compare to tin oxide, though their differences are insignificant. Hence, cow bone could serve well as a good expedient opacifier, with little per cent of zinc oxide to improve the brilliancy.
6. The use of bone ash as part of ceramic glaze material composition has the tendency to check glaze running by the action of the Phosphorous pent oxide which produces a stiff melt.

Conclusion
The research has proved the expedient use of bone ash as opacifier when mixed with transparent glazes. The study further shows that the volume of bone available in abattoirs and those loitering on the streets are enough to be used as opacifier at little or no cost. This could liberate large and small scale ceramic industries, studio potters and
ceramic students in various tertiary institutions to effectively produce opaque glaze, using bone ash as opacifier. This study has also assisted at converting waste that was supposed to have created environmental problem to wealth and subsequently reduced the dependency on tin oxide as ceramic glaze opacifier which is expensive to procure.
Plate 5: Bones after calcination

Plate 6: Crushing of Bones

Plate 7: Grinding of Bones

Plate 8: Charging of bones into mill jar

Plate 9: Placing the jar on a ball mill machine

Plate 10: Test tiles
Plate 11: Brushing glaze samples on test tiles

Plate 12: Glaze samples before firing

Plate 13: Opacified glazed samples produced using cow bone ash with transparent glaze

Plate 13: Results from the firing

Plate 14: Opacified glaze samples produced using tin oxide with transparent glaze
Table 1: Line blend of transparent glaze with cow bone ash

<table>
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<th>98</th>
<th>97</th>
<th>96</th>
<th>95</th>
<th>94</th>
<th>93</th>
<th>92</th>
<th>91</th>
<th>90</th>
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<td>Cow bone ash (%)</td>
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<td>6</td>
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<td>11</td>
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Table 2: Assessment of opacified glaze produced using cow bone ash in term of glaze melt

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Table 3: Assessment of opacified glaze produced using cow bone ash in term of glaze Bloat

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Table 4: Assessment of opacified glaze produced using cow bone ash in term of glaze Crawl

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<td>Frequency</td>
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<td>Percentage</td>
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Table 5: Assessment of opacified glaze produced using cow bone ash in term of glaze opacity.

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<td>Percentage</td>
<td>26.67</td>
<td>20</td>
<td>53.33</td>
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Table 6: Opaque glazes composed and there Assessment

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<tr>
<th>Sample ID</th>
<th>Transparent Glaze (%)</th>
<th>Bone Ash (%)</th>
<th>Zinc Oxide (ZnO)(%)</th>
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<th>Bloat</th>
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Table 7: Assessment of opacified glaze produced using tin oxide in term of glaze melt.

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Table 8: Assessment of opacified glaze produced using tin oxide in term of glaze Bloat.

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Table 9: Assessment of opacified glaze produced using tin oxide in term of glaze Crawl.

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Table 10: Assessment of opacified glaze produced using tin oxide in term of glaze opacity.

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References


